Oligomerization of light olefins in the presence of a supported Brønsted acidic ionic liquid catalyst

Csaba Fehér[a], Szabina Tomasek[b], Jenő Hancsók[b], Rita Skoda-Földes[a,*]

[a] University of Pannonia, Institute of Chemistry, Department of Organic Chemistry, Egyetem u. 10. (P.O. Box 158), H-8200, Veszprém, Hungary
[b] University of Pannonia, Department of MOL Hydrocarbon and Coal Processing, Egyetem u. 10, H-8200, Veszprém, Hungary

ARTICLE INFO

ABSTRACT

Oligomerization of C4-C5 olefins and olefin mixtures has been investigated in the presence of a supported ionic liquid phase (SILP) catalyst, obtained by the physisorption of 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate on silica. Surface properties of the SILP phase were determined from the experimental data of their nitrogen adsorption/desorption isotherms. Fresh and spent catalyst were characterised by ^{13}C- and ^{29}Si-CP MAS NMR spectroscopy and thermogravimetric analysis. Reactivity of alkenes followed the awaited order of isobutene > but-1-ene > pent-1-ene. The main products of oligomerization of hydrocarbon mixtures, modelling the C4-C5 fraction of waste polyethylene cracking products, were isoolefins in the boiling point range corresponding to kerosene fraction components, which is applicable as jet fuel after hydrotreatment. Stability and recyclability of the catalyst could greatly be enhanced by a pretreatment of the fresh catalyst, carrying out an oligomerization experiment with pure isobutene.

1. Introduction

During the past decades the consumption of jet fuels has been constantly growing all over the world. Nowadays the demand of jet fuels is 320 million tonnes, but – based on the forecast – it will grow to 430 million tonnes by 2040 [1]. Together with the increase in the consumption, concerns about fuel price, limited amount of fossil fuels, energy security, emissions, and climate change induced a search for sources alternative to petroleum. Among possible substitutes synthetic fuels, fuels derived from biomass, alcohol fuels, liquid hydrogen or liquid methane have been proposed [2]. The European Union requires the use of 10% fuel derived from renewable sources in the transportation sector by 2020, besides the 2 million tonnes of biojet fuel consumption [3,4].

Alternative jet fuels produced by the hydrogenation of vegetable oils and by Fischer-Tropsch synthesis were approved by ASTM in 2011 and in 2009 [5,6]. These fuels can be mixed with conventional kerosene up to 50%. In jet engines, the use of bioalcohols, such as ethanol and butanol, was also investigated. However, they do not meet the requirements of aircraft operations because of safety and application reasons. Their vapour pressure is high, their flashpoint is low, and thus they cannot be used in aviation [7]. Due to the disadvantages of alcohols, it is probable that hydrocarbons, especially iso- and cycloparaffins bearing good burning properties and low freezing point [8,9], will be

the most suitable components of alternative jet fuel in the future. The main goal is to develop and apply processes which are capable to produce such high energy-content jet fuels with low aromatic content from wastes, residues, non-edible cellulose or lignocellulose containing feedstocks. As an example, biomass can be converted to light olefins through processes such as fermentation, gasification, cracking and deoxygenation [10]. The products can serve as starting material for fuel production via oligomerization or oligomerization/hydrogenation processes.

Polyolefins may serve as another possible source for the generation of light olefins. In the 28 EU member states plus Norway and Switzerland, 60 million tonnes of plastics were produced in 2016, while the world production was 335 million tons. In case of the former group of countries, polyolefins amount to 49.9% of the total production. Accordingly, possible methods for the recycling of waste polyolefines, including their application as starting material for fuel production, are under investigation by several research groups [11].

In the cracking process of waste plastics e.g. waste polyolefines, gases and hydrocarbons with different boiling points and carbon number ranges can be produced. The liquid hydrocarbon fractions cannot be used directly as an engine fuel due to the inadequate oxidation stability of olefinic hydrocarbons. As a consequence, they require additional quality improvement [8,12].

Oligomerization can be a promising process for the upgrading of

---

* Corresponding author.
  E-mail address: skodane@almos.uni-pannon.hu (R. Skoda-Földes).

Table 1
Properties of the silica support and the SILP catalyst.

support or catalyst	S_{BET} [m² g⁻¹]	S_{BJH} (1.7nm-300 nm) [m² g⁻¹]	micropore surface area [m² g⁻¹]	pore volume [cm³ g⁻¹]	D_{mean}[a] [nm]	acid capacity [mmol NH₃ g⁻¹]
silica	467	582	0	0.74	6.1	n.d.
catalyst	238	325	0	0.38	6.3	0.683

[a] average diameter of pores calculated from the values of total pore volumes and surface area.

these high olefin containing fractions. Thus more valuable, higher molecular weight isoolefins are produced from the low value hydrocarbons that can be used – after hydrogenation – as gasoline, jet fuel and diesel fuel blending components [13,14]. Oligomerization can be carried out either in a homogeneous or in a heterogeneous phase in the presence of acidic catalysts [15]. Solid phosphoric acid catalysis has been applied industrially since the early 1930s for the production of gasoline through the oligomerization reaction [16]. The production of solid phosphoric acid catalysts is cheap, but their lifetime is short, and the handling and neutralisation of the deactivated catalyst can cause environmental problems [17,18]. Recently, several solid acid catalysts have been developed to reduce environmental problems associated with acidic catalysis [19]. In oligomerization reactions, zeolites offer possible alternatives to conventional catalysts [20] in industrial procedures, too [16]. However, due to the lower activity of zeolites, their application requires higher temperatures that may result in a rapid decrease in their activity and necessitates a more frequent regeneration process [21]. Also, high temperature may lead to subsequent cracking of oligomers, as it was observed for some zeolites during the oligomerization of 1-pentene [22]. Laboratory experiments were carried out with ion-exchange resin catalysts too. The feedstock of these experiments was composed mainly of model compounds. The ion-exchange resin catalysts are sensitive to high temperature and their thermal stability is not satisfactory, which can cause problems in exothermic processes [23]. Consequently, the development of new types of catalysts can be an important issue.

In the past few years the number of oligomerization experiments carried out with ionic liquids as solvents and/or catalysts has been growing significantly [24]. Ionic liquids are environmentally friendly, so-called 'green' solvents which are not volatile. Their properties can be changed by the proper modification of anions and cations and they can serve as catalysts themselves in a number of organic reactions [25–27]. Chloroaluminate-type Lewis acidic ionic liquids were applied successfully in the oligomerization of C2-C8 alkenes [28–33]. Jet fuel range isoparaffins were obtained from mixtures of gaseous light olefins and hydrogen in the presence of [BMIM][Al₂Cl₇] (BMIM: 1-butyl-3-methylimidazolium) [34]. At the same time, chloroaluminate ionic liquids are extremely moisture-sensitive and easily hydrolyse to release hydrogen chloride in contact with traces of water. Selective dimerization of isobutene could be carried out with the help of more stable Brønsted acidic ionic liquids, such as [MIMBs][OTf] (MIMBs: 1-(4-sulfobutyl)-3-methylimidazolium) [35,36].

However, because of the high viscosity of some ionic liquids, their handling is often cumbersome and catalytic reactions are limited by diffusion processes. These difficulties can be overcome by the use of supported ionic liquid phases (SILP) prepared by the immobilization of ionic liquids on solid supports [37–39]. During our previous work it was shown that silica-supported Brønsted acidic ionic liquid catalysts could be used effectively for the selective trimerization of isobutene [40,41].

Previously, oligomerization of n-olefins with ionic liquid catalysts, such as [MIMBs][OTf] was found to be problematic. Under the same conditions applied for the dimerization of isobutene, isomerization was the main reaction observed for 1-butene, producing 74% of isomers together with 26% of dimers and trimers [36].

Based on the efficiency of the supported version of the catalyst in the reaction of isobutene [40,41], we undertook to explore the applicability of the same methodology in the oligomerization of C4-C5 n-olefins, as well as mixtures thereof. The latter can be considered as simulated C4-C5 hydrocarbon fractions that can be obtained, beside the main products ethylene and propylene, from the cracking of waste polyolefins. The product higher molecular weight isoolefins can be used - after hydrogenation – as jet fuel components.

To the best of our knowledge, there is no example for the application of Brønsted acidic SILP catalysts in the oligomerization of olefin mixtures.

2. Experimental

The conversion and selectivity of the reactions were determined by analysing the composition of the reaction mixtures with GC equipped with a FID detector and 30 m SPB-1 or CHROMPACK 7515 50 m
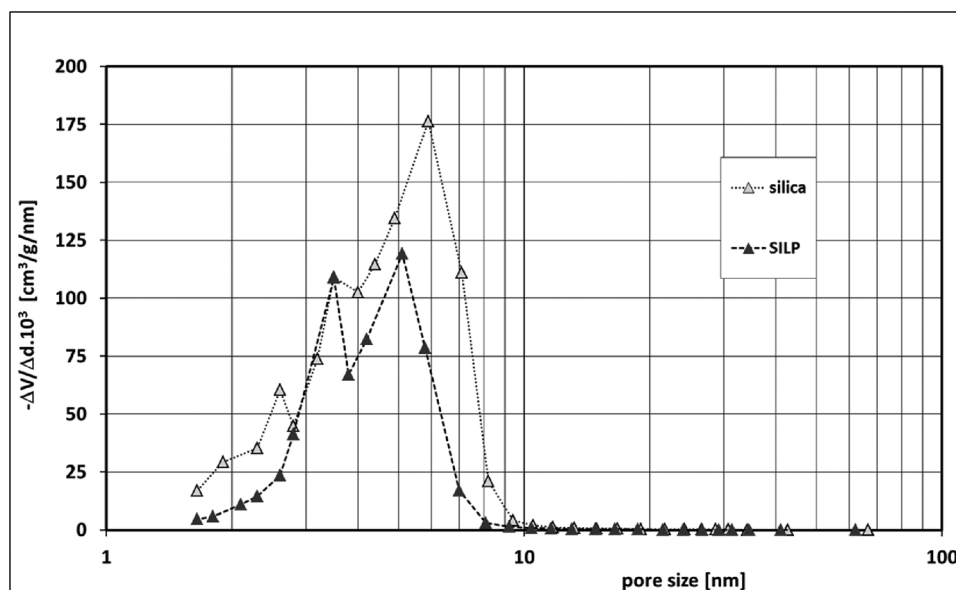

Fig. 1. Differential pore volume distribution of the silica support and the SILP catalyst.
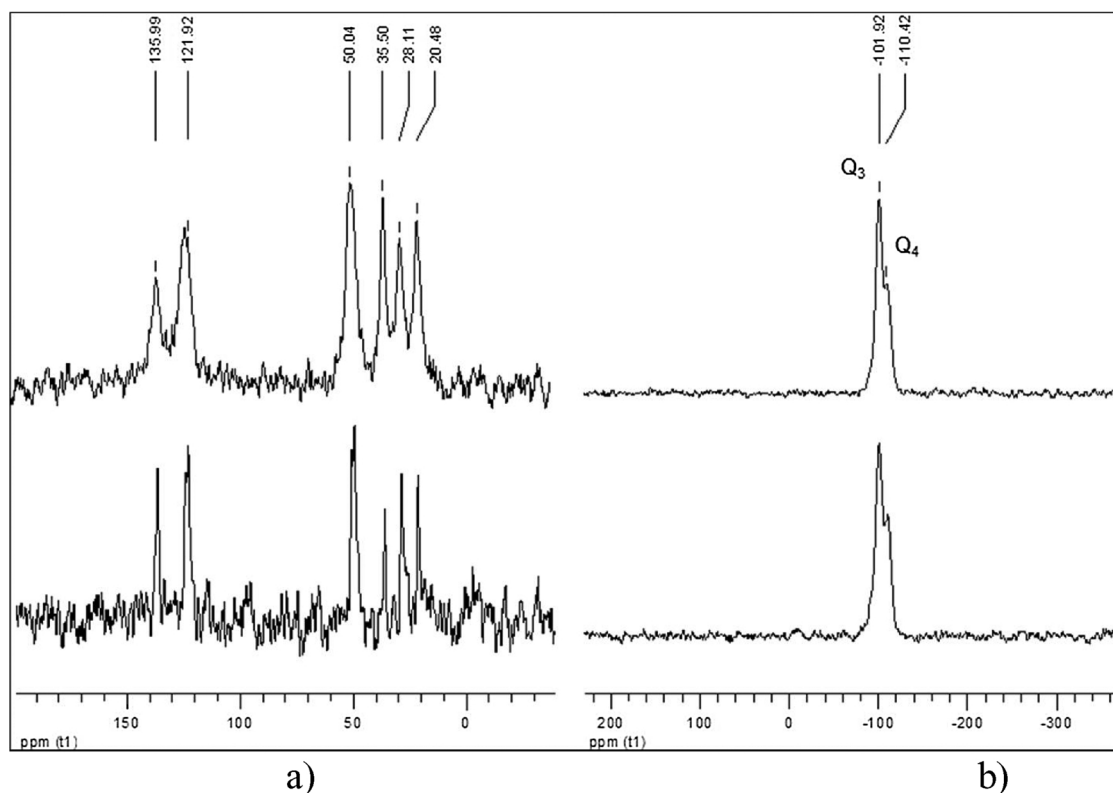
Fig. 2. a) ^{13}C CP MAS NMR spectrum of fresh (below) and spent (above) catalyst. b) ^{29}Si CP MAS NMR spectrum of fresh (below) and spent (above) catalyst.
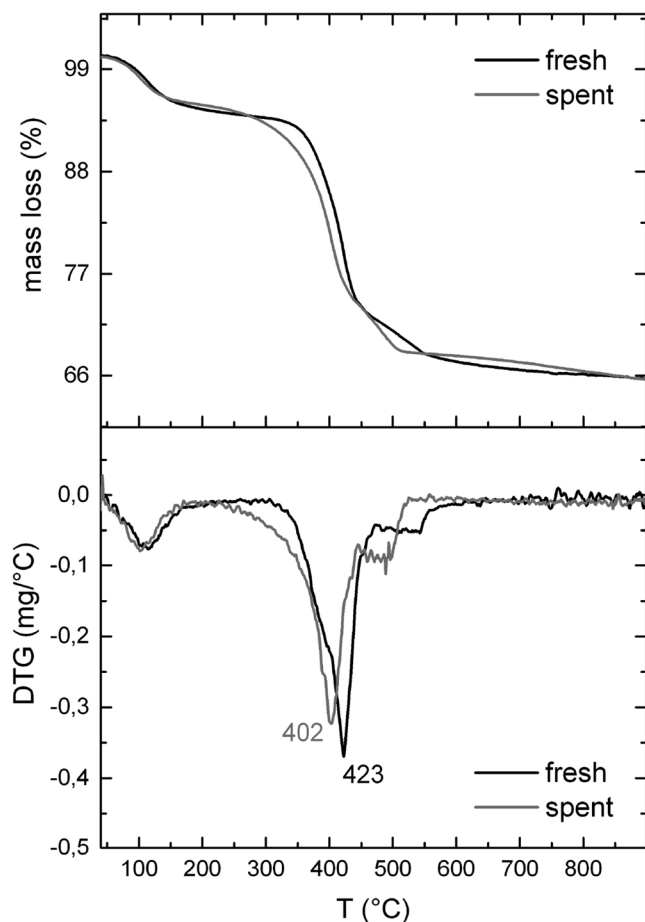

Fig. 3. TGA (above) and DTG (below) curves of fresh and spent catalyst.

columns. The assignment of the chromatographic peaks was carried out by GC–MS measurements (Shimadzu Q2010 Plus gas chromatograph, Shimadzu QP2010 SE mass spectrometer).

Solid phase NMR spectra were recorded on a Bruker Avance 400 spectrometer.

The specific surface area and pore size distribution in the micropore (0–2 nm), mesopore (2–50 nm), and the macropore (50–300 nm) diameter ranges were determined by nitrogen adsorption/desorption isotherms measured with a Micromeritics ASAP 2000-type instrument on samples previously out gassed overnight in vacuum at the temperature of 150 °C. The surface areas of the samples (S_{BET}) were determined by the BET method from the corresponding nitrogen adsorption isotherm. The meso and macropore (2–300 micrometers in diameter) volume values were calculated from the nitrogen desorption isotherms using the BJH (Barret–Joyner–Halenda) theory.

Acidity of the catalyst was determined by means of NH_3 pulse chemisorption at a steady temperature (30 °C) with the aid of a PulseChemisorb type 2705 instrument produced by Micromeritics Instrument Corp.

Thermogravimetric analysis was performed on a Q-1500D instrument (MOM, Budapest, Hungary) (sample weight: 100 mg, heating rate 10 °C / min).

2.1. Preparation of the catalyst

Silica gel was pre-treated by heating for 5 h at 250 °C in vacuo. Then it was allowed to cool to room temperature in a desiccator and was stored under argon. A mixture of silica gel (10 g), the ionic liquid (1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate) [40] (10 mmol) and 25 ml MeOH was stirred at room temperature for 24 h. MeOH was removed in vacuo and the catalyst was dried at 100 °C in vacuo for 5 h to produce the supported ionic liquid. The IL content of the catalyst was 0.86 mmol/ g silica, based on the weight increase of the silica material.

Table 2
Oligomerization of olefins in the presence of the SILP-catalyst[a].

Entry	Olefin	Temp. (°C)	R. time (h)	Conv. (%)[b]	Selectivity (%)[b]				
					Dimer	Trimer	Tetramer	Pentamer	Hexamer
1	isobutene	100	5	100	14	51	33	2	
2	1-pentene	150	5	77	68	23	9		
3	1-pentene	150	10	98	16	27	30	15	12
4	1-pentene[c]	150	10	94	27	30	22	11	10
5	1-butene	150	5	87	46	33	16	5	
6	1-butene[c]	150	10	98	18	31	31	13	7

[a] Reaction conditions: 1g catalyst, 6 ml substrate.
[b] Determined by GC.
[c] With pretreated catalyst.

Table 3
Oligomerization of olefins in the presence of the SILP-catalyst[a].

Entry	Composition of the olefin mixture (ml)			Temp. (°C)	R. time (h)	Conv.[b,c] (%)	Selectivity[b,d] (%)		
	1-pentene	1-butene	iso-butene				< 135 °C	135-270 °C	> 174 °C
1	1	4	1	100	5	34	58	42	32
2[e]	1	4	1	100	5	31	67	33	29
3	1	4	1	150	5	74	42	54	37
4[e]	1	4	1	150	5	68	54	45	26
5[f]	1	4	1	150	5	77	42	51	46
6[e]	1	4	1	150	5	77	42	52	44
7[f]	1	4	1	150	10	93	21	63	67
8[e]	1	4	1	150	10	92	25	63	62
9[g]	1	4	1	150	10	89	28	62	57
10[f]	1	4	1	150	15	98	7	55	88
11[e]	4	1	1	100	5	30	53	47	36
12	1	1	4	100	5	65	29	70	66
13[e]	1	1	4	100	5	69	32	68	66
14	2	2	2	100	5	72	33	64	47
15[e]	2	2	2	100	5	69	38	61	53
16[f]	2	2	2	150	5	81	29	63	50
17[e]	2	2	2	150	5	80	36	58	46
18[f]	1	2.5	2.5	150	5	90	29	64	56
19[e]	1	2.5	2.5	150	5	93	21	67	64
20[g]	1	2.5	2.5	150	5	87	27	64	59

[a] In the presence of 1 g catalyst.
[b] Determined by GC.
[c] Ratio of hydrocarbons > C5.
[d] Selectivity of products with different boiling point range.
[e] 2nd run with the same catalyst.
[f] With pretreated catalyst.
[g] 3rd run with the same catalyst.

2.2. Oligomerization experiments

The reactions were carried out in an autoclave under argon. The autoclave was cooled to −15 °C and the olefin or the hydrocarbon mixture (a total volume of 6 ml) was charged into the reactor, which contained 1 g of the catalyst. The autoclave was pressurised with argon (50 bar, room temperature). The mixture was stirred at 100–150 °C for 5–15 h. The autoclave was cooled to −15 °C, the organic phase was separated and analysed by gas chromatography. The SILP catalyst was washed with pentane (3 × 5 ml), dried in vacuo and reused.

To avoid leaching of the ionic liquid in experiments carried out at high temperature with n-olefins and mixtures containing n-olefins, the catalyst was pretreated by an oligomerization step carried out with isobutene as the starting material. Accordingly, the autoclave was cooled to −15 °C and isobutene (6 ml) was charged into the reactor, which contained 1 g of the fresh catalyst. The autoclave was pressurised with argon (30 bar, room temperature). The mixture was stirred at 100 °C for 5 h. The autoclave was cooled to −15 °C, the organic phase was separated, the SILP catalyst was washed with pentane (3 × 5 ml) and dried at 100 °C in vacuo. This pretreated catalyst was used in the

oligomerization of other subtrates.

3. Results and discussion

3.1. Characterisation of the catalyst

A Brønsted acidic ionic liquid, 1-(4-sulfobutyl)-3-methylimidazo-lium trifluoromethanesulfonate was prepared and immobilized on silica gel by adsorption to give the SILP catalyst as described before [40].

The values of the specific surface area (S_{BET}) and pore volumes of the silica support and the SILP catalyst (Table 1, Fig. 1) were determined from the experimental data of their nitrogen adsorption/desorption isotherms. Assuming that the pores have cylindrical shape, from the values of incremental pore volumes and the average pore diameter, the cumulative surface area (S_{BJH}) can be estimated on the basis of BJH phenomena. As it is expected, there is a loss of BET surface when the support is impregnated with the ionic liquid. Comparing the S_{BET} and S_{BJH} values, it can be assumed that although the total pore volume values decreases because of the active ionic liquid film on the wall of the pores, the pear shaped pores retain their shape during the
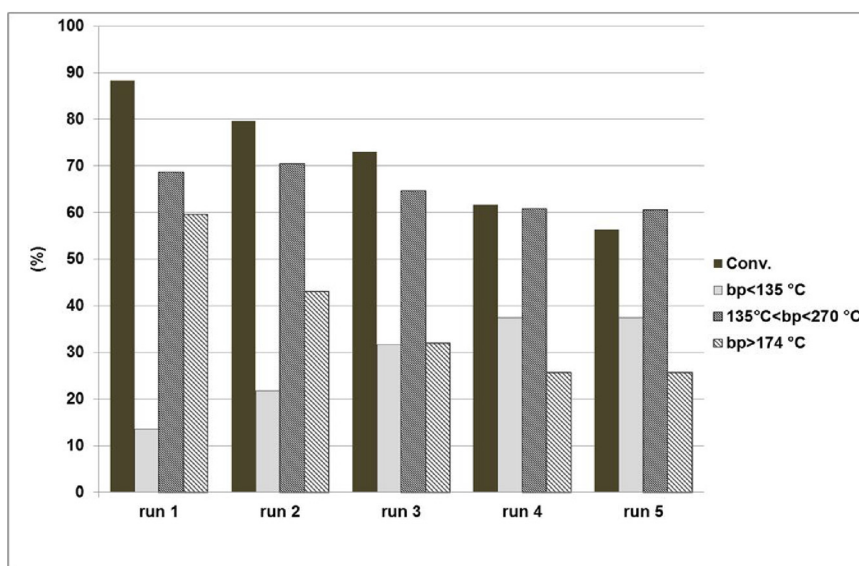
Fig. 4. Conversion (ratio of hydrocarbons > C5) and selectivity of products with different boiling point range in the oligomerization of a mixture composed of 1-pentene/1-butene/isobutene/n-pentane = 4/1/1/3 (ml). Reaction conditions: 150 °C, 15 h, 1 g catalyst.
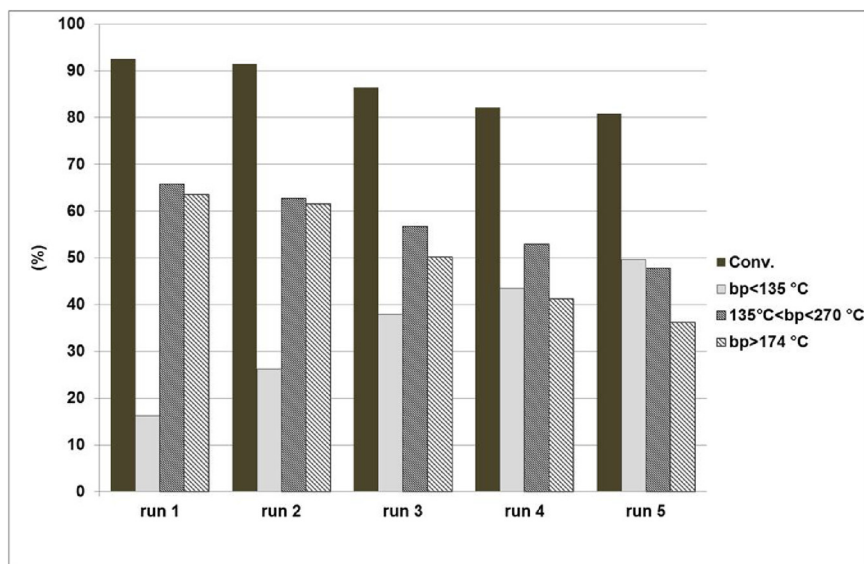

Fig. 5. Conversion (ratio of hydrocarbons > C5) and selectivity of products with different boiling point range in the oligomerization of a mixture composed of 1-pentene/1-butene/isobutene/n-pentane = 1/4/1/3 (ml). Reaction conditions: 150 °C, 15 h, 1 g catalyst.

catalyst preparation process.

In the ^{13}C CP MAS NMR spectrum of the catalyst (Fig. 2a), signals of the carbon atoms of the methyl (35.5 ppm) and butyl groups (20.5 ppm, 28.1 ppm, 50.0 ppm and 50.1 ppm) as well as those assigned to the carbon atoms of the imidazole ring (121.9 ppm, 123.3 ppm and 136.0 ppm) could be distinguished. In the ^{29}Si CP MAS NMR spectrum (Fig. 2b) only the usual signals of the silica support Q_3: $Si(OSi)_3OH$, and Q_4: $Si(OSi)_4$ were observed. The lack of peaks around -60 ppm corresponding to organosiloxane moieties shows that no covalent bonds were formed between the ionic liquid and the support. Aside from some broadening of the signals in the ^{13}C CP MAS NMR spectrum, no change was observed in the spectra of the spent catalyst used in the oligomerization of isobutene.

Thermogravimetric analysis proved the stability of the catalyst below 300 °C (Fig. 3) and there was only a little change in its thermal behaviour after use.

3.2. Oligomerization of olefins and olefin mixtures

Previously, we reported on the oligomerization of isobutene in the presence of supported ionic liquid catalysts prepared by the adsorption of ionic liquids on silica [40,41]. In order to broaden the scope of the procedure, we decided to explore the possibility of the conversion of olefinic hydrocarbons, obtainable in the cracking process of waste polyolefines, into high value isoolefins. During the experiments 1-butene and 1-pentene, as well as mixtures of C4-C5 hydrocarbons, modelling the same fraction of pyrolysis of polyethylene [42–44] were used as the starting material.

First the catalyst, 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate supported on silica, was used for the conversion of 1-butene and 1-pentene (Table 2). As it was expected, 1-pentene and even 1-butene showed lower reactivity compared to isobutene. Contrary to the oligomerization of isobutene (entry 1), the reactions of these olefins led to the corresponding dimers as the main products and they could not be completed in 5 h even at a higher temperature
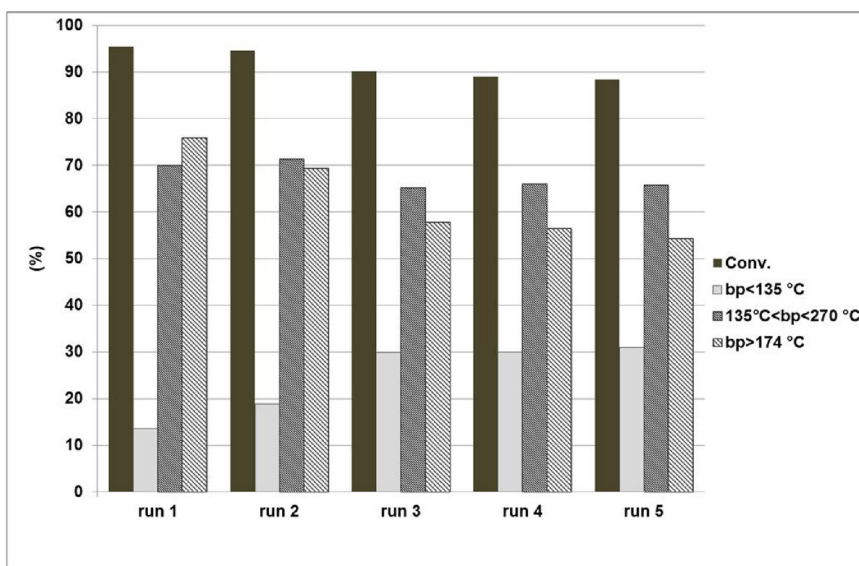
Fig. 6. Conversion (ratio of hydrocarbons > C5) and selectivity of products with different boiling point range in the oligomerization of a mixture composed of 1-pentene/1-butene/isobutene/n-pentane = 1/1/4/3 (ml). Reaction conditions: 150 °C, 15 h, 1 g catalyst.
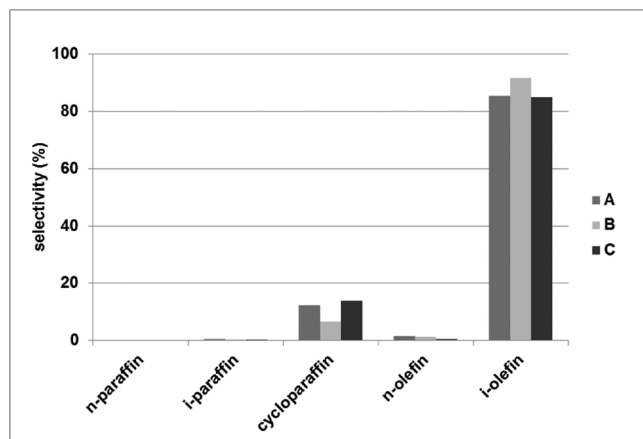

Fig. 7. Product distribution (average value of 5 runs) in the oligomerization of different hydrocarbon mixtures (A: 1-pentene/1-butene/isobutene/n-pentane = 4/1/1/3 (ml); B: 1-pentene/1-butene/isobutene/n-pentane = 1/4/1/3 (ml); C: 1-pentene/1-butene/isobutene/n-pentane = 1/1/4/3 (ml). Reaction conditions: 150 °C, 15 h, 1 g catalyst.

Table 4
Composition of unreacted n-olefins in the oligomerization mixtures[a].

starting mixture	ratio of n-butenes (%)[b]			ratio of n-pentenes (%)		
	trans-2-C4	*cis*-2-C4	1-C4	*trans*-2-C5	*cis*-2-C5	1-C5
A	60	32	8	72	25	3
B	61	31	8	72	24	4
C	60	32	8	71	25	4

[a] A: 1-pentene/1-butene/isobutene/n-pentane = 4/1/1/3 (ml); B: 1-pentene/1-butene/isobutene/n-pentane = 1/4/1/3 (ml); C: 1-pentene/1-butene/isobutene/n-pentane = 1/1/4/3 (ml). Reaction conditions: 150 °C, 15 h, 1 g catalyst.
[b] Determined by GC(CHROMPACK 7515 50 m column), average value of 5 runs.

(150 °C) (entries 2, 5). Although the application of a longer reaction time improved the conversion of 1-pentene (entry 3), it resulted in the formation of a two-phase liquid mixture at the end of the reaction due to the desorption of the ionic liquid from the support under these

conditions. (It should be mentioned that no leaching was observed in the five-hour-long reactions.) Interestingly, the leaching of the catalyst could be prevented by a pretreatment step. This involved the oligomerization of isobutene carried out at 100 °C for 5 h in the presence of the freshly-made catalyst before its use for the conversion of another olefin or olefin mixture. Although except for some broadening of the signals, no change could be observed in the ^{13}C- and ^{29}Si NMR spectra of the SILP catalyst (Fig. 2) no loss of the ionic liquid could be observed in any of the further reactions, and good conversion of 1-pentene and 1-butene could be achieved in 10 h (entries 4, 6). This shows that oligomerization of the highly reactive isobutene promote the formation of a stable film of the ionic liquid on the support that is a prerequisite to produce a catalyst with good recyclability. The importance of pretreatment was proved before even in the oligomerization of isobutene with ionic liquid catalysts immobilized on microporous silica supports [41].

Based on the selectivity data given in Table 2 it can be stated after hydrogenation the dimer and trimer products, generally formed in the greatest amount, as well as low boiling fraction of tetramers obtained from butenes, can be applied as jet fuel blending components after hydrogenation. Additionally, the other part of the tetramers (C16 with higher boiling point as well as C20 obtained from 1-pentene), the pentamers and the hexamers can be used as diesel fuel blending components.

The pretreated catalyst was used efficiently in the oligomerization of 1-pentene/1-butene/isobutene mixtures with different compositions (Table 3). In order to investigate the effect of pretreatment, the activity of the original catalyst was also checked in some of the experiments carried out at lower temperature and/or with shorter reaction time.

As the C4-C5 fraction of polyethylene cracking contains n-butenes as the main components [42], a detailed investigation of the effect of the reaction conditions on the outcome of oligomerization was carried out using an olefin mixture with the composition of 1-pentene/1-butene/isobutene = 16.5/67/16.5 (v/v%) (Table 3 entries 1–10).

Although no leaching of the ionic liquid could be observed at either of the temperatures investigated, only low or moderate conversion could be achieved using a short reaction time (5 h) together with a selectivity between 33–54% toward jet fuel range products (135 °C < bp < 270 °C, entries 1–4). Pretreatment was found to increase the stability of the catalyst unequivocally. Although there are no great differences between the conversions (entries 3–6), the increase in the selectivity for low boiling point products in the second run using the
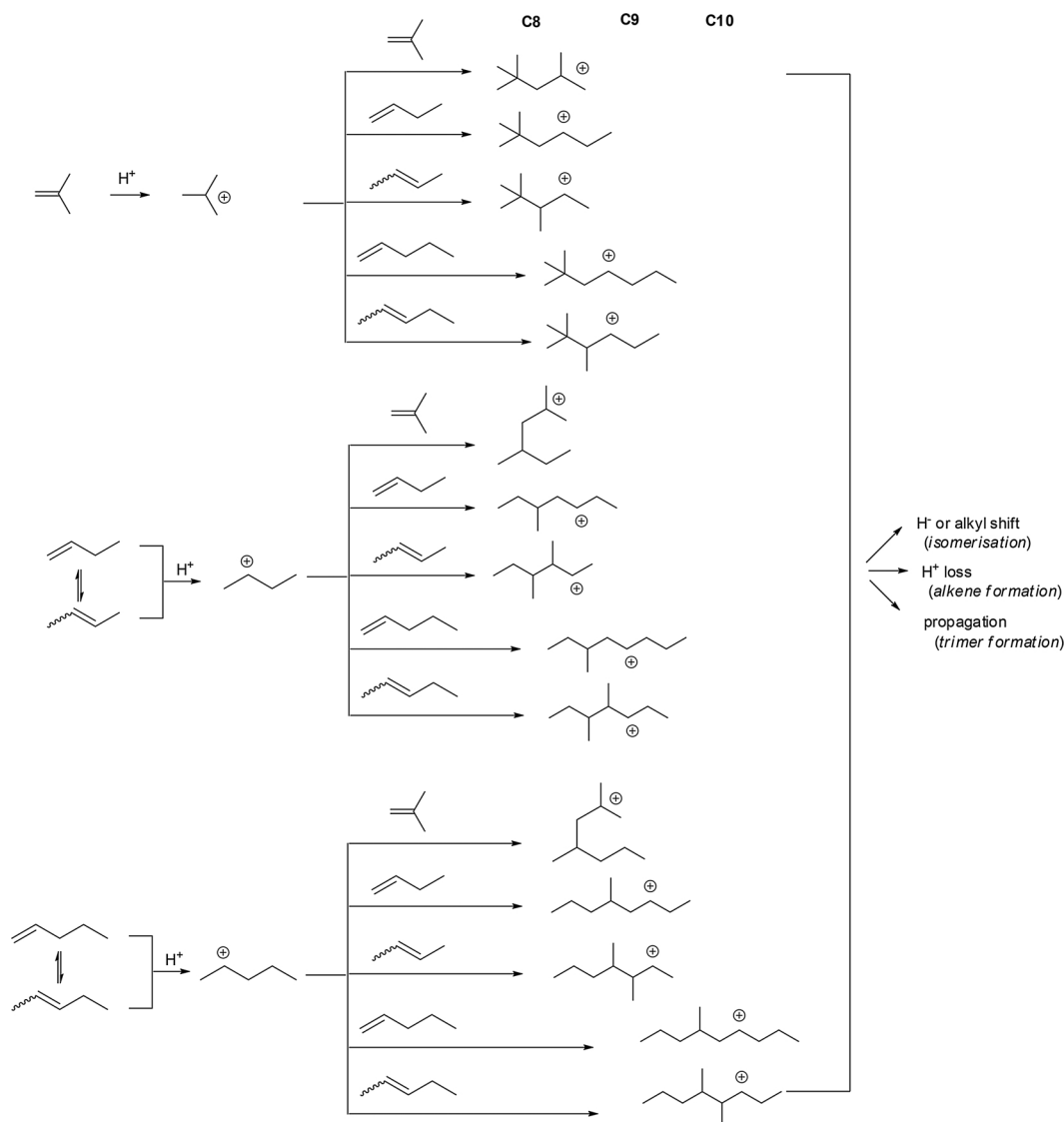
Scheme 1. The first reaction steps of the oligomerization of 1-pentene/1-butene/isobutene mixtures.

untreated catalyst (entries 2, 4) evidently shows some loss of activity.

The application of longer reaction times improved the conversion (entries 7–10), and pushed the selectivity towards higher molecular weight oligomers. This results in a decrease in the selectivity for products that can be used as precursor for jet fuel in the 15-hour-long reaction (entry 10). At the same time, under the optimal conditions (150 °C, 10 h), the pretreated catalyst exerted a stable performance even upon recycling, leading to high conversion and acceptable selectivity (entries 7–9).

Investigation of mixtures with other compositions showed that in accordance with the results obtained for pure olefins, only low conversion and low selectivity for higher oligomers could be achieved starting from an 1-pentene rich material (entry 11). On the contrary, mixtures with high isobutene content led to higher conversion (entries 12–19) and improved selectivity for products in the boiling point range of 135–270 °C even in reactions at lower temperature (entries 12–15). Oligomerization of the starting material with 1-butene and isobutene as the main components resulted in excellent conversion and good yield (64–67%) of target products in 5 h-long reactions (entries 18–20) even with the spent catalyst (entries 19, 20).

3.3. Oligomerization of olefin mixtures containing saturated hydrocarbons

As the light fraction of products obtained by polyethylene cracking contains saturated hydrocarbons, catalytic activity of the SILP catalyst was tested in mixtures containing n-pentane beside the olefins 1-pentene, 1-butene and isobutene (Figs. 4–6). Because of the lower concentration of olefins in the starting material, a longer reaction time (15 h) had to be used to achieve good conversion. Oligomerizations were carried out with the pretreated catalyst in all cases.

In accordance with the previous results, the lowest conversion could be achieved with the starting material rich in 1-pentene (Fig. 4). Although the selectivity for the jet-fuel range products (135 °C < bp < 270 °C) was above 60% a considerable loss of activity was observed upon the reuse of the catalyst.

The most stable performance with only a small loss of activity, together with a good selectivity towards the products in the boiling point range of 135 °C–270 °C was observed in the mixture rich in isobutene (Fig. 6).

The main products were isoolefins in all of these oligomerization reactions (Fig. 7). The formation of cycloparaffins, useful components of fuels without the necessity of further upgrading, was also detected in considerable amounts (5–15%). The selectivity for these types of products did not change considerably upon catalyst reuse.

Isobutene was almost totally consumed in all reactions and was detected only in traces in the products. At the same time, a detailed GC–MS investigation of the reaction mixtures revealed an isomerisation reaction of n-olefins prior to oligomerization. Unreacted C4-C5 olefins were found to be mainly 2-alkenes (Table 4). The ratio of *trans-* and *cis-* 2-enes did not change considerably either upon the reuse of the catalyst or the application of mixtures of different compositions as the starting material. *Trans* isomers prevailed over the *cis* derivatives in each case.

Oligomerization of 1-pentene/1-butene/isobutene mixtures may result in product mixtures with a great diversity of structure (Scheme 1). Protonation of the monomers in the presence of the acidic catalyst and subsequent reaction of the cations with monomers lead to carbenium ions with 8–10 carbon atoms. The latter may undergo isomerisation via hydride (or alkyl) shift before a further reaction step. Loss of a proton leads to C8-C10 alkene formation. Trimers may be formed directly via propagation from the carbenium ions or via protonation of the primarily formed dimeric alkenes and subsequent reaction with a monomer.

The presence of cycloalkanes might be due to a partial cracking of the products. Formation of monomethyl- and polymethyl-substituted cyclopentanes and cyclohexanes from alkenes with at least six carbon atoms was observed on zeolites at high temperatures. Exact structures of the compounds and the mechanism leading to them are unknown [45]. In the present case, the acidity of the SO_3H group seems to lead to similar reactions even at lower temperatures.

In case of the widely used zeolite catalysts, the presence of mesopores was found to be essential for good selectivity towards oligomerization [46,47]. To improve mass transport, such mesoporous zeolites can be obtained by desilication/dealumination or by the construction of nanosized zeolite crystals with sufficient porosity [48]. The SILP phase, apllied as catalyst in the present work, was found to retain the mesoporous structure of the support after the immobilisation of the ionic liquid.

With zeolite catalysts, 21–75% selectivity (for products in the boiling point range of 177–343 °C) was observed between reaction temperatures of 140–250 °C [20]. Dimerization, leading to products corresponding to naphtha, was found to be the main reaction during oligomerization of 2-butene [49] and 1-pentene [50] at 150 °C and 200 °C, respectively. The SILP catalyst was used successfully for the synthesis of products with higher boiling point range even at 150 °C reaction temperature.

In contrast to the [MIMBs][OTf] ionic liquid [36], oligomerization was found to be the main reaction even in case of 1-butene and 1-pentene in the presence of the supported catalyst.

Moreover, the methodology may offer a further possibility of fine tuning both the porosity of the support and the structure of the supported ionic liquid to improve results. Although at present the catalyst has been tested in batch reactions, its application under flow conditions is also possible.

4. Conclusions

The SILP catalyst, obtained by the physisorption of 1-(4-sulfobutyl)-3-methylimidazolium trifluoromethanesulfonate on silica, could be used efficiently in the oligomerization of C4-C5 olefins of hydrocarbon mixtures, which correspond to the composition of the C4-C5 fraction of the thermal cracking of polyolefines (e.g. PE). The main products were isoolefins in the boiling point range corresponding to kerosene components, which can be applied as jet fuel blending components after hydrogenation. Stability of the catalyst could greatly be enhanced by a pretreatment of the fresh catalyst, carrying out an oligomerization experiment with pure isobutene. Moreover, the best catalyst recycling could be achieved starting from an isobutene-rich hydrocarbon mixture. It has been shown that the catalytic system is suitable to produce isoolefins, that can be converted to high quality engine fuel blending components, starting from feedstocks originated from waste polyolefines.

References

[1] World Oil Outlook, Organization of the Petroleum Exporting Countries, Vienna (2014), pp. 216–244 2014.
[2] C. Zhang, X. Hui, Y. Lin, C.-J. Sung, Renew. Sust. Energ. Rev. 54 (2016) 120–138.
[3] Directive 2009/28/EC of the European Parliament and of the Council, (2009).
[4] D. Chiaramonti, M. Prussi, M. Buffi, D. Tacconi, Appl. Energy 136 (2014) 767–774.
[5] T.K. Hari, Z. Yaakob, N.N. Binitha, Renew. Sust. Energ. Rev. 42 (2015) 1234–1244.
[6] Gevo's Alcohol-to-jet Fuel Meets Approved ASTM Standard, (2016) 28.03 http://www.biomassmagazine.com (Accessed on 22 March 2018).
[7] S.P. Srivastava, J. Hancsók, Fuels and Fuel-Additives, John Wiley & Sons, Inc., Hoboken, New Jersey, 2014, pp. 290–293.
[8] Z. Eller, Z. Varga, J. Hancsók, Fuel 182 (2016) 713–720.
[9] J.I. Hileman, R.W. Stratton, Transp. Policy (Oxf) 34 (2014) 52–62.
[10] V. Zacharopoulou, A.A. Lemonidou, Catalysts 8 (1) (2018) 2.
[11] Plastics – the Facts 2017. An analysis of European plastics production, demand and waste data. http://www.plasticseurope.org (Accessed on 26 March 2018).
[12] D. Sági, P. Solymosi, A. Holló, Z. Varga, J. Hancsók, Energy Fuels 32 (2018) 3519–3525.
[13] E. Kriván, Sz. Tomasek, J. Hancsók, J. Clean. Prod. 136 (2016) 81–88.
[14] C.P. Nicholas, Appl. Catal. A Gen. 543 (2017) 82–97.
[15] G.A. Olah, A. Molnár, Hydrocarbon Chemistry, second ed., John Wiley & Sons, Inc, Hoboken, New Jersey, 2003, pp. 723–806.
[16] H. Olivier-Bourbigou, A. Forestiére, L. Saussine, L. Magna, F. Favre, F. Hugues, Oil Gas Eur. Mag. 36 (2010) 97–102.
[17] S. Raseev, Thermal and Catalytic Processes in Petroleum Refining, Taylor & Francis, 2003, pp. 539–557.
[18] N.M. Whitton, US Patent No. 4742032 (1988).
[19] P. Gupta, S. Paul, Catal. Today 236 (2014) 153–170.
[20] O. Muraza, Ind. Eng. Chem. Res. 54 (2015) 781–789.
[21] J.W. Yoon, S.H. Jhung, J.-S. Chang, Bull. Korean Chem. Soc. 29 (2008) 339–341.
[22] A. Kulkarni, A. Kumar, A.S. Goldman, F.E. Celik, Catal. Commun. 75 (2016) 98–102.
[23] E. Kriván, J. Hancsók, Top. Catal. 58 (2015) 939–947.
[24] Cs. Fehér, E. Kriván, Z. Eller, J. Hancsók, R. Skoda-Földes, C. Lesieur (Ed.), The Use of Ionic Liquids in the Oligomerization of Alkenes, InTech, Rijeka, 2014, pp. 30–67.
[25] R. Ratti, H. Shirota (Ed.), Ionic Liquids: Synthesis and Applications in Catalysis, Advances in Chemistry, 2014 Article ID 729842.
[26] R.L. Vekariya, J. Mol. Liq. 227 (2017) 44–60.
[27] J. Lunagariya, A. Dharb, R.L. Vekariya, RSC Adv. 7 (2017) 5412–5420.
[28] M. Goledzinowski, V.I. Birss, Ind. Eng. Chem. Res. 32 (1993) 1795–1797.
[29] O. Stenzel, R. Brüll, U.M. Wahner, R.D. Sanderson, H.G. Raubenheimer, J. Mol. Catal. A Chem. 192 (2003) 217–222.
[30] A.G. Azizov, E.S. Kalbalieva, R.V. Alieva, N.R. Bektashi, B.M. Aliev, Pet. Chem. U S S R 50 (2010) 56–64.
[31] A.H. Azizov, R.V. Aliyeva, E.S. Kalbaliyeva, M.J. Ibrahimova, Appl. Catal. A Gen. 375 (2010) 70–77.
[32] M.D. Ibragimova, F.I. Samedova, R.Z. Gasanova, N.G. Azmamedov, E.Z. Eivazov, Pet. Chem. U S S R 47 (2007) 61–66.
[33] S. Yang, Z. Liu, X. Meng, C. Xu, Energy Fuels 23 (2009) 70–73.
[34] P. Jiang, X. Wu, L. Zhu, F. Jin, J. Liu, T. Xia, T. Wang, Q. Li, Energ. Convers. Manag. 120 (2016) 338–345.
[35] L. Magna, J. Bildé, H. Olivier-Bourbigou, T. Robert, B. Gilbert, Oil Gas Sci. Technol. Rev. IFP 64 (2009) 669–679.
[36] Y. Gu, F. Shi, Y. Deng, Catal. Commun. 4 (2003) 597–601.
[37] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, Top. Catal. 40 (2006) 91–102.
[38] R. Skoda-Földes, Molecules 19 (2014) 8840–8884.
[39] R.L. Vekariya, A. Dharc, J. Lunagariya, Compos. Interfaces 24 (2017) 801–816.
[40] Cs. Fehér, E. Kriván, J. Hancsók, R. Skoda-Földes, Green Chem. 14 (2012) 403–409.
[41] Cs. Fehér, E. Kriván, J. Kovács, J. Hancsók, R. Skoda-Földes, J. Mol. Catal. A Chem. 372 (2013) 51–57.
[42] J. Mosio-Mosiewski, M. Warzala, I. Morawski, T. Dobrzanski, Fuel Process. Technol. 88 (2007) 359–364.
[43] A. Marcilla, M.I. Beltrán, R. Navarro, Appl. Catal. B 86 (2009) 78–86.
[44] G. Elordi, M. Olazar, G. Lopez, M. Amutio, M. Artetxe, R. Aguado, J. Bilbao, J. Anal. Appl. Pyrolysis 85 (2009) 345–351.
[45] Y.V. Kissin, Catal. Rev. 43 (2001) 85–146.

[46] B. Chiche, E. Sauvage, F. Di Renzo, I.I. Ivanova, F. Fajula, J. Mol. Catal. A Chem. 134 (1998) 145–157.

[47] C. Bertrand-Drira, X. Cheng, T. Cacciaguerra, P. Trens, G. Melinte, O. Ersen, D. Minoux, A. Finiels, F. Fajula, C. Gerardin, Microporous Mesoporous Mater. 213 (2015) 142–149.

[48] R. Chal, C. Gérardin, M. Bulut, S. van Donk, ChemCatChem 3 (2011) 67–81.

[49] J.A. Martens, R. Ravishankar, I.E. Mishin, P.A. Jacobs, Angew. Chem. Int. Ed. 39 (2000) 4376–4379.

[50] A. Corma, C. Martínez, E. Doskocil, J. Catal. 300 (2013) 183–196.